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JCS26 U.S. PTO  
09/137127  
08/20/98

In re Patent Application of

WARD et al

Serial No. Unassigned

Filed: June 29, 1998

For: COMPACTED BIOMATERIALS

Atty. Ref.: 604-451

Group:

Examiner:



\* \* \* \* \*

August 20, 1998

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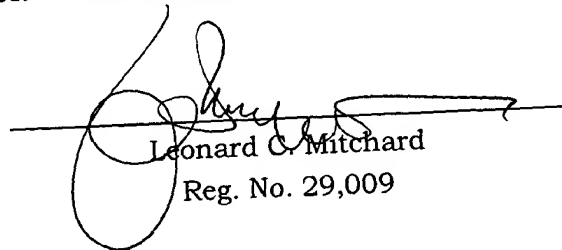
It is respectfully requested that this application be given the benefit of the foreign filing date under the provisions of 35 U.S.C. §119 of the following, a certified copy of which is submitted herewith:

<u>Application No.</u>	<u>Country of Origin</u>	<u>Filed</u>
9600800.8	Breat Britain	15 January 1996 And 30
9611249.5	Great Britain	May 1996

Respectfully submitted,

**NIXON & VANDERHYE P.C.**

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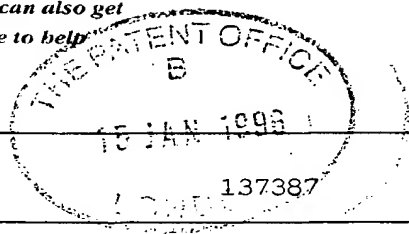


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06512123001 a

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4. Title of the invention

COMPACTED BIOMATERIALS

5. Name of your agent (if you have one)

A P DOLAN

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Claim(s)

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Statement of inventorship and right to grant of a patent (Patents Form 7/77)

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Date 15 JANUARY 1996

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### COMPACTED BIOMATERIALS.

The present invention relates to novel composite materials, to a process for production of such materials and to their use as structural materials, particularly in prostheses but also in other non-physiological situations.

5        Hydroxyapatite (HA) reinforced high density polyethylene (PE) composite (HAPEX) was pioneered as a bone substitute by Bonfield et al. (see GB 2085461 B) who demonstrated that an optimum combination of mechanical and biological performance is produced by HA content in the region of 40 vol %. This amount of reinforcement was shown to result in a bone substitute with a stiffness and strength suitable for minor load  
10    bearing applications. However, for major load bearing skeletal implants considerably higher stiffness and strength are required, comparable with the values associated with cortical bone.

      Molecular orientation in a polymer leads to a significant enhancement in the stiffness and strength along the orientation direction (I.M. Ward, "The preparation, structure  
15    and properties of ultra-high modulus flexible polymers", Advances in Polymer Science, vol. 70, pp. 1-70, 1985).

      It is desirable to have methods for the production of suitable structural materials, and particularly bio-structural materials, with the purpose of achieving increased bio-compatible filler content, particularly HA content for higher bioactivity, and better  
20    mechanical properties.

      The present inventors have now provided such a method having the basic concept of combining polymeric fibres, preferably of polyolefins such as PE, with fillers, particularly biocompatible fillers such as HA, to produce structural materials, particularly bone analogues, by replacing the previously used isotropic polymer with polymeric fibre,  
25    particularly high modulus polyolefin fibre such as polyethylene (HMPE) fibres, and compressing this mixture using hot compaction. Preferably the fibre is used as pieces of fibre in chopped fibre form.

      Hot compaction is a process which allows the production of large section polymeric products with substantial fibre morphology content, retaining to a large extent the high

stiffness and strength associated with fibres (see GB 2253420 and US Serial No.07/934,500 derived from PCT/GB92/00401), particularly high modulus fibres.

The present method is of particular interest in the fabrication of HA/PE composites having a fibre morphology matrix, using chopped HMPE fibres. The present inventors  
 5 have further found, surprisingly, that such a material is amenable advantageously to hydrostatic extrusion, a technology never before attempted with hot compacted fibres. While the present method may be preferentially applied to such polymers, it may also be applied to other oriented polymers such as vinyls, polyesters, polyamides, polyetherketones and polyacetals such as vinyl chlorides, vinyl fluorides, vinylidene fluorides, PHB, PEEK,  
 10 polyoxymethylenes and all the other materials referred to as suitable for hot compaction use in PCT/GB92/00401.

Thus in a first aspect of the present invention there is provided a composite material comprising an inorganic filler material and a fibrous polymeric material characterised in that the fibrous material has areas of adjacent fibres fused together to form a continuous  
 15 matrix while retaining fibrous structure in the composite.

Preferably the fused fibres are oriented. Preferably the inorganic filler is a particulate filler. Examples of fillers include talc, mica, graphite, metal oxides, metal hydroxides and metal carbonates. Most preferably the inorganic filler is a biocompatible material, such as for example an apatite, eg. hydroxyapatite.

20 The composite material is preferably of extruded form and particularly a hydrostatically extruded form.

Preferred composite materials of the invention have a flexural modulus between 7 and 30 GPa, preferably greater than 10 GPa, still more preferably having a flexural modulus greater than 12 GPa, most preferably greater than 15 GPa.

25 Preferred composite materials of the invention have a flexural strength between 50 and 150 Mpa, more preferably greater than 60 Mpa, still more preferably greater than 80 Mpa and most preferably greater than 100 MPa.

Preferred composite materials of the invention have a flexural ductility between 0.5 and 10 %, more preferably, between 0.5 and 7%, most preferably between 0.5 and  
 30 4%.

Preferably the fibrous polymeric material is a polyolefin, preferably polypropylene



or polyethylene, most preferably polyethylene, and most preferably is in a high modulus form.

In a second aspect of the invention there is provided a method for producing a composite material from an inorganic filler material and a fibrous polymeric material including the steps of mixing and heating the filler material and fibrous polymeric material characterised in that it comprises (i) mixing the materials and maintaining the mixture at a contact pressure such that at least some of the fibres are in intimate contact with each other, (ii) heating the mixture so maintained at a temperature and for a time such as to melt no more than a part of the fibre surface area then (iii) compressing the heated mixture at a compaction pressure.

Preferably the part of the fibre surface area that melts is from 5 to 95% of the fibre surface area, more preferably from 5 to 50% of the surface area.

Preferably the material is cooled such that on cooling the melted part of the fibrous polymeric material forms a three dimensional matrix binding the fibrous material and filler material together. The mixture is preferably maintained at a temperature at least that which an extrapolation of the leading edge of the endotherm of the fibrous material measured by differential scanning calorimetry intersects the temperature axis.

Preferably the temperature at which the mixture is maintained is less than the peak temperature of melting of the polymer fibres as measured by differential scanning calorimetry.

The mixture is preferably maintained at 0.5 to 4 MPa during step (i) and step (ii) prior to compressing at a compaction pressure; still more preferably between 0.5 and 2 MPa prior to compressing at a compaction pressure.

The material preferably comprises oriented polymer fibres, preferably in the form of continuous fibres that have been chopped into smaller lengths.

The temperature at which the mixture is maintained is preferably at between 1 and 10°C below the melting point of the polymeric material, more preferably between 1 and 5°C below the melting point of the polymeric material.

In a preferred method of the invention the compacted material produced in step (iii) is subjected to extrusion, more preferably hydrostatic extrusion. The product from step (iii) or the extrusion step is advantageously powderized then reprocessed as in steps (i) to (iii).

Preferably the reprocessed material is then subjected to extrusion, preferably hydrostatic extrusion.

The hydrostatic extrusion step is preferably performed by (iv) placing a billet of the material in contact with a die orifice while being surrounded by a fluid medium, (v) heating then fluid and the billet to a temperature below the melting point of the polymeric component of the material and (vi) applying pressure to the fluid such as to cause the billet to be extruded through the die.

Preferably the die is a convergent die, more preferably having an extrusion ratio of extruded product 3:1 or more, more preferably 7:1 or more and most preferably at least 11:1.

Preferably the fluid used in the hydrostatic extrusion is an oil.

Preferably the compaction pressure used in step (iii) is from 5 to 1000MPa, more preferably 20 to 500 Mpa, and most preferably from 40 to 80MPa.

Preferably the polymer is a homo or co-polymer of a polyolefin, more preferably having a weight average molecular weight of 50,000 to 3,000,000 and most preferably from 500,000 to 3,000,000.

The fibre is preferably gel or melt spun fibre.

The composites of the invention are preferably used in or as prostheses, and particularly bone replacement prostheses.

The method and materials of the present invention will now be described by way of illustration only by reference to the following non-limiting Examples. Further embodiments falling within the scope of the invention will occur to those skilled in the art in the light of these.

## EXAMPLES

### 25 EXPERIMENTAL

#### Materials

HA is a synthetic calcium phosphate ceramic  $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})]$  supplied by Biotol Ltd., UK. Grade P88 was chosen for the present work, with  $4.14 \mu\text{m}$  average size<sup>(8)</sup>. Chopped HMPE fibres were supplied by Hoechst Celanese Research Co. (Summit, NJ, USA), from continuous fibres manufactured by SNIA Fibres (Cesano Maderno, Italy).

Some samples also contained a third type of material, namely 40 vol % HA/60 vol % PE composite produced with the melt compounding technology, as seen in a previous publication<sup>(8)</sup>. The polymer was Rigidex HM 4560 PX (BP Chemicals Ltd., UK) whilst the HA was P88 grade.

5            Table 1 gives the main parameter values characterising the PEs and HA used in this work.

## METHODOLOGY

### Preparation of Composites

The HA particles and chopped fibres were mixed at room temperature with a domestic appliance, namely a Braun Hand Blender MR 350 and the chopper HC accessory (Braun (UK) Ltd., London). This equipment was found particularly convenient because the handheld motor casing and the chopper are both axially aligned, allowing the blending to be carried out at an inclined angle while rolling the lower end on the bench. This procedure assisted the movement of the fibres inside the containers and avoided agglomeration. The chopper accessory was modified to improve efficiency, namely a) a second pair of blades was added midway along the shaft, b) the nylon bearings were replaced by ball bearings, and c) the plastic base was replaced by a heavier aluminium base. Mixing of about 59 of chopped fibres plus the required amount of HA was carried out for about 3 minutes using the three available motor speeds and rest periods in a reproducible sequence.

The composites were compacted in an aluminium mould placed in a hydraulic hot press. The mould produced samples of rectangular cross section and 150 x 10 mm L x W. Maximum thickness was 8 mm. The temperature during compaction was monitored with a probe connected to an electronic thermometer. 5 mm of the sensing end of the probe could be inserted with a tight fit into holes bored at various points around the mould. The space between the hot plates of the press was shielded from the outside with Perspex sheets. With these arrangements a predetermined moulding temperature (usually around 135°C) in the middle of the mould could be achieved within 0.2°C, whilst the gradient between the two ends of the mould was 0.5°C.

The blended material inside the mould was maintained at the predetermined temperature for 20 minutes under a small pressure (approximately 100psi = 0.69MPa) to ensure good thermal contact between the mould and the two hot plates of the press. The compression load was then increased rapidly to 9 tonne giving a compaction pressure of about 60MPa, followed by switching the heating off and water cooling of the hot press. The mould reached a temperature of 50°C in about 30 minutes, when it was left on a bench to cool down to room temperature before removing the sample.

Some samples were powderised to improve the HA distribution within the polymeric matrix. The powderising process included three stages a) crushing in a fly press, b) chopping with a Kenwood Chef Food Mixer fitted with the spice mill attachment (Kenwood Ltd., Havant, Hampshire, UK), and c) powderising proper in a  
5 Fritsch Pulverisette 14 Rotor-Speed Mill (Fritsch GmbH, Idai-Oberstein, Germany) using progressively finer sieves from 6 mm down to, when required, 80  $\mu\text{m}$ . The Rotor-Speed Mill was fitted with a 12 knives stainless rotor and the speed used was 16,000 r.p.m.

Powderising could be readily achieved down to a 1 mm sieve. Finer sieves required considerable care owing to heat generation. The material to be fed into the Rotor-Speed  
10 mill was kept in a beaker, which was itself immersed in liquid nitrogen. However, no liquid nitrogen was poured into the machine.

After powderising, the material was re-compacted. At this stage it was necessary to re-melt the polyethylene fraction which melted during the first compaction, but without affecting the fraction with fibre morphology. This was achieved by re-compacting at 3°C  
15 to 4°C lower than the temperature used during the first compaction (the HMPE fibres melt at about 140°C, which compares with  $\approx 130^\circ\text{C}$  for isotropic PE<sup>(25)</sup>).

In some cases, composites were prepared in a somewhat different way, namely the chopped HMPE fibres were blended with a mixture of HA and compacted, 40 vol % HA/60 vol % PE composite. The latter was prepared as seen in a previous  
20 publication<sup>(8)</sup> and was available in coarse powder form. The HA and compounded composite were blended in a Waring 8011G Rotary Blender (Waring Products Div., Dynamics Corporation of America, Connecticut, 06057, USA) fitted with the stainless steel mini container MC3. The mixing was carried out using a reproducible sequence of blending pulses (15 seconds), tapping and scrubbing the containers floor with a metal  
25 spatula. The powder thus obtained was compressed in a stainless steel mould placed in a hydraulic press. The procedure for this stage was similar to that followed for the production of compacted fibre composites, as seen above, except that the moulding temperature was 180°C and the samples were cylindrical rods 60 mm x 12 mm or 60 mm x 18 mm, L x diameter. For convenience this material will be referred to as  
30 "enriched" compounded composite (ECC).

The rods of "enriched" compounded composite were powderised as seen above and blended with the chopped HMPE fibres following a similar technique as used for the HA/chopped fibre system. The proportion of the various materials used was chosen such that the final mix achieved the predetermined HA content, while two thirds of the PE had  
 5 fibre morphology.

#### Hydrostatic Extrusion

Details of the experimental procedure may be seen in a previous publication<sup>(30)</sup> and only a brief summary will be presented here.

The die used had a cone semiangle of 15° and the bore diameters were 1.8 mm, 2.5  
 10 mm or 3.5 mm, according to the extrusion ratio (ER) and the original dimensions of the compacted bars of composite to be extruded. Billets were machined from the bars with a 15° nose to create an initial pressure seal. At the end of the nose a constant diameter stub was also machined, which protruded a few millimetres through the die. A cable attached to the stub was used to drive a rotary potentiometer to provide a displacement signal which  
 15 was recorded from the beginning of the extrusion (this was the first time that the HE process was monitored from its initial stages). A haul off load of 100 g was attached to the free end of the cable to ensure a firm drive of the rotary potentiometer. The back 3 mm of the billet was machined to a larger diameter to act as a plug and prevent the violent release of pressure at the end of a run.

20 The pressurising fluid was castor oil (J. L. Seaton, Hull, UK). The billets were coated with two layers of Evostick (Evoke Ltd., UK) to avoid direct contact between the polymer matrix and the pressurising fluid, which involves a risk of stress cracking<sup>(30)</sup>. It was found that the Evostick coating peeled off during extrusion and did not go through the die.

25 After preliminary trials, the extrusion temperature was fixed at 115°C. The extrusion pressure was a function of the material and the extrusion ratio (ER, ratio of the initial and final cross sections). There was little control of the extrusion rate, which was about 1.5 mm min<sup>-1</sup>.

### Differential Scanning Calorimetry (DSC)

The effect of the various processing stages (blending, compaction, powderising, re-compaction and HE) on the morphology of the PE matrix was qualitatively assessed by studying the melting behaviours of the material. For this purpose, a Perkin Elmer  
 5 Differential Scanning Colorimeter DSC7 (Perkin Elmer Corp., Norwalk, Connecticut, USA) was used with a scanning rate of 10°C and 2 to 10 mg of material for each run.

### Scanning Electron Microscopy (SEM)

The effect of the various processing stages on the dispersion of HA in the PE matrix was assessed with SEM techniques. The specimen preparation procedures consisted of  
 10 sectioning, moulding in an acrylic resin, grinding on silicon carbide papers from grade 220 down to 1000 grit, polishing using alumina powders with a particle size of 5, 1 and 0.3 µm progressively, cleaning in an ultrasonic bath to remove the alumina powder from the polished surface, drying with compressed air and gold coating with a thickness of approximately 20 nm. The polished surfaces were examined under a JEOL 6300 SEM

### 15 Mechanical Testing:

The mechanical properties of the composites were assessed in tensile (T) and flexural (F, three point bending) mode of deformation. In each case three main constants were measured; modulus (TM and FM), strength (TS and FS) and ductility (TD and FD). All the mechanical tests were carried out at room temperature (22 + 1.50°C) using an  
 20 Instron machine (Instron Ltd., High Wycombe, UK).

#### a. Tensile Measurements:

Two types of geometries were used, bars with rectangular cross sections (compacted samples) and cylindrical rods (i.e. compacted and hydrostatically extruded samples). The rectangular bars were machined following ISO specifications<sup>(31)</sup> (Figure 2). The cylindrical  
 25 rods were machined according to ASTM specifications<sup>(32)</sup> (Figure 3). The tensile test parameters are given in Table 2, where the gauge length is the separation of the spring-loaded extensometer knives used to measure the deformation. Note in particular that the moduli were calculated at small strain and, therefore, they represent the resistance of the material to initial deformation. Other characteristics of the tests are:-

1) For the determination of TM of rectangular bars, four cycles of loading and unloading were performed, the first of which was ignored because it was occasionally irregular (probably due to the extensometer knives settling down on the sample). The other three were very reproducible and the results were averaged to calculate the TM value.

5        2) Cylindrical rods were loaded only once up to fracture. The extensometer was removed from the specimen when the strain reached 1.0% and thereafter the strain was calculated from the crosshead displacement. Cylindrical rod specimens slipped in the grips before failure. This problem was overcome by embedding the ends of the samples in an epoxy resin before testing.

#### 10        b. Flexural Measurements

Rectangular bars and cylindrical rods were tested in three point bending using identical parameters. These are shown in Table 3. Broadly, plates were tested following ASTM 790<sup>(33)</sup> recommendations, while rods were tested with their original extruded diameters.

15        The formulae used to calculate the various flexural properties are those obtained from the simple beam theory<sup>(34)</sup>. For convenience, these are shown in Table 4. Note that the terms "strain" and "ductility" refer to the maximum strain (in %) in the sample at a given deflection. For all the samples the following conditions applies:

$$\frac{\text{Gauge length}}{\text{Thickness}} \geq 10$$

20

As required by the simple beam theory in order to neglect shear deformation.

Some rods did not break in bending but, instead, the load deflection ??? exhibited a yield point. Unless otherwise stated, FD was measured as the maximum strain at the deflection, after the yield point, giving 25% decrease from maximum load.



All materials produced were evaluated in terms of their flexural stiffness, strength and ductility. A qualitative assessment of the effect of the various processing stages on the matrix morphology was made with differential scanning calorimetry (DSC). The dispersion of the filler, ie. HA in the fibre matrix, ie. chopped PE, was studied with  
5 scanning electron microscopy (SEM) technique.

TABLE 1

## MATERIAL CHARACTERIZATION

<b>HA (P88)</b>	
Density (g/cm <sup>3</sup> )	3.156
Particle size (μm)	4.14*
<b>HMPE Fibre</b>	
Density (g/cm <sup>3</sup> )	0.960
$\overline{M}_w$	130.000
$\overline{M}_N$	12.000
DR	30:1
Diameters (μm)	13
Tensile modulus (GPa)	40
Tensile strength (GPa)	1.3
Fracture strain	5%
Segment length of choopped fibre (mm)	3.5
<b>Rigidex HM 4560XP</b>	
Density (g/cm <sup>3</sup> )	0.945
$\overline{M}_w$	350.000
$\overline{M}_N$	
Tensile modulus (GPa)	0.68
Tensile strength (MPa)	23.5
Fracture strain %	>300

\* From ref. (8)

TABLE 2  
TENSILE TEST PARAMETERS

TEST	GAUGE LENGTH (mm)		INITIAL SEPARATION BETWEEN GRIPS (mm)		CROSSHEAD SPEED (mm/min)		PROPERTY CALCULATED AT STRAIN %	
	RECTANGULAR BARS	CYLINDRICAL RODS	RECTANGULAR BARS	CYLINDRICAL RODS	RECTANGULAR BARS	CYLINDRICAL RODS	RECTANGULAR BARS	CYLINDRICAL RODS
TM	25	5.45	50	19	0.5	0.5	0.1	0.05
TS,TD	25	-	50	19	0.5	0.5	-	-

TABLE 3

FLEXURAL TEST PARAMETERS

TEST	LOADING/ SUPPORTING RODS DIAMETER  (mm)	GAUGE LENGTH+  (mm)	NOMINAL SAMPLE DIMENSIONS  (mm)			CROSSHEAD SPEED  (mm/min)	PROPERTY CALCULATED AT STRAIN  (%)
			LENGTH	CROSS SECTION			
				RECTANGULAR BARS	CYLINDRICAL RODS		
FM <sub>130</sub>	25/12	130	150	10 x 2	As Extruded	2.0	0.03
FM <sub>50</sub>	10/10	50	7.5			0.5	0.03
FS/FD	10/10	50	7.5			2.0	-

+ Distance between the supporting rods

**TABLE 4**  
**SIMPLE BEAM THEORY FORMULAE FOR**  
**THREE POINT BENDING**

	RECTANGULAR BARS	CYLINDRICAL RODS
FM	$\frac{1}{4} \frac{WL^3}{\delta bd^3}$	$\frac{4}{3} \frac{WL^3}{\pi \delta D}$
FS	$\frac{3}{2} \frac{WL}{bd^2}$	$\frac{8WL}{\pi d^3}$
MAXIMUM STRAIN	$6 \frac{d\delta}{L^2}$	$\frac{6D\delta}{L^2}$
SYMBOLS	W = Load $\delta$ = Deflection L = Gauge Length d = Sample Thickness b = Sample Width	W = Load $\delta$ = Deflection L = Gauge Length d = Diameter of Overall Sample D = Diameter of Gauge Length

TABLE 5

## MECHANICAL PROPERTIES OF HA/PE COMPOSITES WITH FIBRE MATRIX MORPHOLOGY

SYSTEM	HA CONTENT	OTHER MATERIALS	POWDERIZ.  mm	COMPACT. TEMP(S)  °C	ER	MECHANICAL PROPERTIES					
						TENSILE			FLEXURE		
						TM GPa	TS MPa	TD %	FM GPa	FS MPa	TD %
100% Fibre	-	-	-	136.4	-	4.0±1.5	25±2	>10	-	-	-
			2	138.0/133.0	-	2.9±0.2	19±0	1.8±0.2			
			1	138.0/133.0	-	2.5±0.3	14±2	1.2±0.2			
			0.5	138.0/133.0	-	2.7±0.4	20±3	3.3±2.5			
HA/ Chopped Fibre	20	-	-	137.4	-	7.1±0.7	15±1	>1			
	30	-	0.5	138.0/133.6	-	5.6±0.5	22±1	>1			
			6	138.2/134.0	4:1	-	27	>1			
					7:1	4.6	14	>1			
			0.5	138.2/133.4	4:1	8.3	76	1.2			
					7:1	14.0	73	1.2	16.1±1.5	104±1	6.9±0.1
					11:1	-	-	-	19.4±0.6	117±5	6.0±0.5

TABLE 5 (continued)

## MECHANICAL PROPERTIES OF HA/PE COMPOSITES WITH FIBRE MATRIX MORPHOLOGY

SYSTEM	HA CONTENT	OTHER MATERIALS	POWDERIZ.  mm	COMPACT. TEMP(S)  °C	ER	MECHANICAL PROPERTIES					
						TENSILE			FLEXURE		
						TM GPa	TS MPa	TD %	FM GPa	FS MPa	T %
"Enriched" Betol/Chopped Fibre	vol %										
	30	Betol 40HA/60PE+	-	137.7	-	7.0±0.2	18±0	>1	6.1±0.1	46±6	3.2±1.0
		HA to 60HA/40PE	0.5	137.4/132.5	-	4.4±0.2	17.5±0.1	>1	-	-	-
	40	Betol 40HA/60PE+ HA to 70HA/30PE	-	137.9	-	7.9	20	>1	-	-	-
	50	Betol 40HA/60PE+	0.08	138.0/133.1	7:1	-	-	-	12.4±0.6	72	2.8*
		HA to 75HA/25PE			11:1	-	-	-	13.5±0.2	69±11	1.6*±0.9
	Cortical Bone					7-30	50-150	0.5-3.0			
Compounded 40HA/60PE (Betol Material)						4.3±0.2	20.7±1.6	2.6±0.4	4.1±0.3	32±10	1.6*±0.1

\* Break at maximum load (see text for definition of FD)

Example 2: Hydroxyapatite/High Modulus Polyethylene fibre composite.

HA particles and chopped HMPE fibres were mixed at room temperature with a modified domestic hand blender. The composites were compacted in an aluminium mould placed in a hydraulic hot press with preliminary experiments showing that compaction  
 5 temperatures of between 137.0°C and 138.0°C are adequate to melt a small proportion of the fibre surface, as described in GB 2253420, and form a continuous network of re-crystallized PE binding the fibres and the HA particles together

Some samples were powderized after compaction with the purpose of improving the HA distribution within the polymeric matrix. The material was re-compacted at  
 10 about 3.0°C-4.0°C lower than the first compaction temperature, ensuring the re-melting of the PE fraction melted during the first compaction, but without affecting the fraction retaining the fibre morphology (the HMPE fibres melt at  $\approx$ 140°C, which compares with  $\approx$ 130°C for the re-crystallized PE).

In some cases the composites were prepared in a somewhat different way,  
 15 namely by blending the HMPE chopped fibres with a mixture of HA and HAPLEX (40 vol % HA)]. This mixture is referred to as "enriched" HAPLEX. The proportions of the various materials used were chosen such that the final mix had the predetermined HA content, with two-thirds of the PE having fibre morphology.

20 Example 3: Hydrostatically extruded hot compacted composite

The hydrostatic extrusion process [A.G. Gibson and I.M. Ward, "Hydrostatic extrusion of linear polyethylene: effects of molecular weight and product diameter", J. Polym. Sci., Polym. Phys. Ed., vol. 16, pp. 2015-3030, 1978] used a billet of the composite surrounded by a fluid which was heated up below its melting point. The billet was made to pass  
 25 through a convergent die by the application of a back pressure to the fluid. The extrusion ratio (ER) is defined as the ratio of the cross section area of the billet to that of the die bore. It was found that powderizing and re-compaction were necessary requirements for the successful hydrostatic extrusion of HA/chopped HMPE fibre composites.

The mechanical properties of the composites were assessed in three point bending.



Three measurements were undertaken, namely flexural modulus (FM), flexural strength (FS) and flexural ductility (FD). The term "ductility" refers to the maximum strain (in %) in the sample at the deflection producing failure.

#### Properties:

5           Tables 6a and 6b give the main flexural properties of HA/chopped HMPE fibre composites. For comparison, some results obtained with other materials are also included. All the hydrostatically extruded composites achieve the levels of stiffness and strength associated with cortical bone. On the other hand, none of the composites without hydrostatic extrusion possess properties comparable to the biological tissue.

10           When comparing the system without hydrostatic extrusion, Table 1a shows that the properties of HAPLEX are broadly matched by the properties of HA/chopped fibre composites. However, after hydrostatic extrusion these systems are distinctly superior to extruded HAPLEX (Table 6b).

15           SEM observations with polished samples showed that HAPLEX has a highly homogeneous distribution of HA particles in the polymeric matrix, whereas HA/chopped fibre composites have regions with varying degrees of HA content. Powderizing and re-compaction of the HA/chopped fibre systems significantly improved their HA distribution and these stages were required for successful hydrostatic extrusion, as noted above.

20           Table 1a shows that powderizing and recompaction of HA/chopped fibre composites are accompanied by a reduction in their stiffness and strength. This can be attributed to damage of the fibre morphology taking place during the powderizing stage, as shown by DSC studies, which also reveal that a high melting point morphology (fibre morphology) is re-established during the hydrostatic extrusion process, accounting  
25           for the superior properties of these systems (Table 6b).

          Thus these results show that hydrostatic extrusion of hot compacted HA/chopped HMPE fibre composites which have been powderized and re-compacted provides the highest stiffness and strength yet encountered with HA/PE bone substitute material, fully comparable with the values associated with cortical bone.

Table 6. Flexural properties of extruded and non-extruded HA/chopped HMPE fibre composites of the invention.

a) Non-extruded (Example 2)

HA content [ vol %]	Powderizing [mm]	FM [GPa]	FS [MPa]	FD [%]
Cortical bone	-	7-30	50-150	0.5-3.0
HAPEX	-	4.7	32	1.4
0	-	3.9	54	4.2
	0.5	2.4	19	0.9
20	-	5.8	49	2.8
	0.5	3.6	41	2.7
30*	-	5.5	47	2.3
	0.5	4.2	38	1.9

b) Hydrostatically extruded (Example 3).

HA content [ vol %]	ER	FM [GPa]	FS [MPa]	FD [%]
HAPEX [8]	8:1	8.8	81	5.5
0	4:1	6.9	88	6.0
	7:1	12.7	103	3.9
20	7:1	15.2	119	3.6
30	4:1	9.3	86	3.4
	7:1	15.5	104	3.0
	11:1	19.5	117	2.8
30*	4:1	9.0	75	3.6
	7:1	11.9	87	3.3
40	4:1	10.8	86	3.8
	7:1	14.1	97	3.8
50*	7:1	12.4	72	2.8
	11:1	13.5	67	1.6

\* For these systems the HA was incorporated as "enriched" HAPEX.

CLAIMS.

1. A composite material comprising an inorganic filler material and a fibrous polymeric material characterised in that the fibrous material has areas of adjacent fibres fused together to form a continuous matrix while retaining fibrous structure in the composite.
2. A composite material as claimed in claim 1 wherein the fused fibres are oriented.
3. A composite material as claimed in claim 1 or 2 wherein the inorganic filler is a particulate filler.
4. A composite material as claimed in any one of claims 1 to 3 wherein the filler is selected from talc, mica, graphite, metal oxides, metal hydroxides and carbonates.
5. A composite material as claimed in any one of claims 1 to 4 wherein the inorganic filler is a biocompatible material.
6. A composite material as claimed in claim 5 wherein the biocompatible material is an apatite.
7. A composite material as claimed in claim 6 wherein the apatite is hydroxyapatite.
8. A composite material as claimed in any one of claims 1 to 7 wherein the material is of extruded form.
9. A composite material as claimed in claim 8 wherein the material is in hydrostatically extruded form.
10. A composite material as claimed in any one of claims 1 to 9 having flexural modulus between 7 and 30 GPa.

11. A composite material as claimed in claim 10 having flexural modulus between greater than 10 GPa.
12. A composite material as claimed in claim 10 having a flexural modulus greater than 12 GPa.
- 5 13. A composite material as claimed in claim 10 having a flexural modulus greater than 15 GPa.
14. A composite material as claimed in any one of claims 1 to 13 having a flexural strength between 50 and 150 MPa.
15. A composite material as claimed in claim 14 having a flexural strength greater than  
10 60 MPa.
16. A composite material as claimed in claim 14 having a flexural strength greater than 80 MPa.
17. A composite material as claimed in claim 14 having a flexural strength greater than 100 MPa.
- 15 18. A composite material as claimed in any one of claims 1 to 17 having a flexural ductility between 0.5 and 10 %.
19. A composite material as claimed in claim 18 having a flexural ductility between 0.5 and 7%.
20. A composite material as claimed in claim 19 having a flexural ductility between  
20 0.5 and 4%.

21. A composite material as claimed in any one of the preceding claims wherein the fibrous polymeric material is a polyolefin.
22. A composite material as claimed in claim 21 wherein the polyolefin is polyethylene.
23. A composite material as claimed in claim 21 wherein the polyethylene is of high modulus.
24. A method for producing a composite material from an inorganic filler material and a fibrous polymeric material including the steps of mixing and heating the filler material and fibrous polymeric material characterised in that it comprises (i) mixing the materials and maintaining the mixture at a contact pressure such that at least some of the fibres are in intimate contact with each other, (ii) heating the mixture so maintained at a temperature and for a time such as to melt no more than a part of the fibre surface area then (iii) compressing the heated mixture at a compaction pressure.
25. A method as claimed in claim 24 wherein the part of the fibre surface area that melts is from 5 to 95% of the fibre surface area.
26. A method as claimed in claim 25 wherein the part of the fibre surface area is from 5 to 50% of the surface area.
27. A method as claimed in claim 24 wherein the compressed mixture is cooled such that on cooling the melted part of the fibrous polymeric material forms a three dimensional matrix binding the fibrous material and filler material together.
28. A method as claimed in any one of claims 24 to 27 wherein the mixture is maintained at a temperature at least that which an extrapolation of the leading edge of the endotherm of the fibrous material measured by differential scanning calorimetry intersects the temperature axis.

29. A method as claimed in claim 28 wherein the temperature at which the mixture is maintained is less than the peak temperature of melting of the polymer fibres as measured by differential scanning calorimetry.
30. A method as claimed in any one of claims 24 to 29 wherein the mixture is  
5 maintained at 0.5 to 4 MPa during step (i) and step (if) prior to compressing at a compaction pressure.
31. A method as claimed in claim 30 wherein the mixture is maintained at between 0.5 and 2 MPa prior to compressing at a compaction pressure.
32. A method as claimed in any one of claims 24 to 31 wherein the fibrous material  
10 comprises oriented polymer fibres.
33. A method as claimed in any one of claims 24 to 32 wherein the fibres are in the form of continuous fibres that have been chopped into smaller lengths.
34. A method as claimed in any one of claims 24 to 33 wherein the temperature at  
15 which the mixture is maintained is between 1 and 10°C below the melting point of the polymeric material.
35. A method as claimed in claim 34 wherein the temperature is between 1 and 5°C below the melting point of the polymeric material.
36. A method as claimed in any one of claims 24 to 35 wherein the compacted material  
20 produced in step (iii) is subjected to extrusion.
37. A method as claimed in claim 36 wherein the extrusion step is carried out by hydrostatic extrusion.

38. A method as claimed in claim 36 or 37 wherein the product from step (iii) or the extrusion step is powderized then reprocessed as in steps (i) to (iii).
39. A method as claimed in claim 38 wherein the reprocessed material is then subjected to extrusion.
- 5 40. A method as claimed in claim 39 wherein the extrusion is hydrostatic extrusion.
41. A method as claimed in claim 36 or claim 40 wherein the hydrostatic extrusion step is performed by (iv) placing a billet of the material in contact with a die orifice while being surrounded by a fluid medium, (v) heating then fluid and the billet to a temperature below the melting point of the polymeric component of the material, (vi) applying pressure to the  
10 fluid such as to cause the billet to be extruded through the die.
42. A method as claimed in claim 41 wherein the die is a convergent die.
43. A method as claimed in claim 41 or 42 wherein the extrusion ratio of the extruded product is 3:1 or more.
44. A method as claimed in claim 43 wherein the extrusion ratio is 7:1 or more.
- 15 45. A method as claimed in claim 44 wherein the extrusion ratio is at least 11:1.
46. A method as claimed in any one of claims 42 to 45 wherein the fluid is an oil.
47. A method as claimed in any one of claims 24 to 46 wherein the compaction pressure used in step (iii) is from 5 to 1000MPa.
48. A method as claimed in claim 47 wherein the compaction pressure used in step (iii)  
20 is from 20 to 500 Mpa.

49. A method as claimed in claim 48 wherein the compaction pressure is from 40 to 80MPa.
50. A composite or method as claimed in any one of claims 1 to 49 wherein the polymer is a homo or co-polymer of a polyolefin.
- 5 51. A composite or method as claimed in claim 50 wherein the polymer has a weight average molecular weight of 50,000 to 3,000,000.
52. A composite or method as claimed in claim 51 wherein the polymer has a weight average molecular weight of 500,000 to 3,000,000.
53. A composite or method as claimed in any one of claims 47 to 52 wherein the fibre  
10 is gel or melt spun fibre.
54. A structural material comprising a composite as claimed in or provided by a method as claimed in any one of the preceding claims.
55. A prosthesis comprising a material as claimed in claim 54.



## ABSTRACT

### COMPACTED BIOMATERIALS

A composite material comprising an inorganic filler material and a fibrous polymeric material characterised in that the fibrous material has areas of adjacent fibres fused together  
5 to form a continuous matrix while retaining fibrous structure in the composite.

